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# Adsorption of F127 onto single-walled carbon nanotubes characterised using small-angle neutron scattering

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## Abstract

Aqueous single-walled carbon nanotube dispersions are often made using polymers from the Pluronic family of amphiphilic block copolymers, however relatively few studies have been made using small-angle neutron scattering techniques to discover the mechanism by which they act. SANS results reported here show that a relatively simple core-shell cylinder model can be used to fit data successfully at different contrasts. The results across all contrasts showed that the best fit gave an inner nanotube radius of 10 Å, corresponding to small nanotube bundles with a small amount of water present

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(20%), and a polydisperse adsorbed layer thickness of 61 Å, with a water content of 94% in the adsorbed layer. The data fitting is thus consistent with a small SWCNT bundle surrounded by an extended and water-swollen F127 adsorbed layer. Comparing the scattering from F127/SWCNT at different contrasts, it has been found that the polymer-decorated SWCNTs are contrast matched at a D<sub>2</sub>O/H<sub>2</sub>O volume ratio of 0.36:0.64, corresponding to a scattering length density of  $1.92 \times 10^{-6} \text{ Å}^{-2}$ .

## Introduction

Carbon nanotubes have been of great interest since their discovery by Iijima in 1991, due to their unique properties such as their high aspect ratio, mechanical strength and electrical conductivity.<sup>1</sup> Single-walled carbon nanotubes (SWCNTs) can be thought of conceptually as a rolled-up sheet of atomically-thin carbon, with both the angle used when rolling up this cylinder and the diameter of the resulting nanotube being key parameters in determining its electronic properties. Syntheses of SWCNTs result in a third of the nanotubes being metallic, with two thirds being semiconducting.<sup>2</sup> There has been a surge in research interest in recent years looking into possible separation methods for these two species of nanotube in order to make SWCNTs of a single electronic type for future electronic applications.

A major challenge in utilising the properties of SWCNTs is the difficulty encountered on attempting to form a nanotube dispersion in either aqueous or organic media, due to the propensity of SWCNTs to bundle together. Methods which have been investigated to overcome this problem include both covalent and non-covalent approaches, with non-covalent methods generally being favoured as they do not affect the intrinsic properties of the SWCNTs.

A variety of both small molecule and polymeric surfactants have been reported as forming SWCNT dispersions successfully. Interactions between surfactant molecules and the SWCNT surface occur with the adsorption of the hydrophobic tail of the surfactant onto the SWCNT wall. Although such dispersants are commonly used with SWCNTs, relatively few

studies have utilised small-angle neutron scattering (SANS) as a technique to investigate the adsorption of surfactants onto SWCNTs. Yurekli et al. studied the adsorption of sodium dodecyl sulphate (SDS) on CNTs at low surfactant concentration using SANS and reported that the adsorption of SDS molecules on the SWCNT surface was unstructured, with no preferential adsorption of either the headgroup or the tail of the molecule onto the SWCNT wall.<sup>3</sup> Theoretical calculations have shown that in dilute solution, the adsorption of surfactant on the tube is random in nature, while at high surfactant concentration hemispherical micelles are preferentially formed.<sup>4</sup> The stabilisation of carbon black and SWCNTs has been reported to be more effective with the use of surfactants possessing aromatic groups, due to  $\pi$ - $\pi$  stacking interactions between the surfactant and the graphitic carbon surface.<sup>5,6</sup>

Work published by Granite et al. looked into using SANS to probe the interactions between SWCNTs and Pluronic block copolymers (F127 and F108) below the polymers' critical micellisation temperature (CMT).<sup>7</sup> They observed minimum scattering at 70% D<sub>2</sub>O, rather than the 17% D<sub>2</sub>O, which is where the Pluronic polymers would be expected to be “matched out” based on their chemical structure. Both a cylindrical core-adsorbed chains model and a cylindrical core-shell-chains model were reported as fitting the data well, however corrections had to be made as to why the data at 70% D<sub>2</sub>O scattered less than the data at 40% D<sub>2</sub>O, a value which is closer to the match point of F127.

We have studied the adsorption of F127 onto SWCNTs using SANS, and have found our data to show a different scattering vector ( $Q$ ) dependency to previous data. Our data show minimal scattering at a D<sub>2</sub>O/H<sub>2</sub>O composition consistent with a model in which the SWCNT has a high scattering length density, and is surrounded by a diffuse F127 adsorbed layer. We have found it possible to obtain good fits to our F127/SWCNT data using a relatively simple core-shell cylinder model.

# Experimental

## Materials

Single-walled carbon nanotubes (SWCNTs) synthesised by a high pressure carbon monoxide (HiPCO) method were purchased from NanoIntegris (“purified” grade). F127 was obtained from BASF (Ludwigshafen, Germany). D<sub>2</sub>O was purchased from Sigma Aldrich (99.9 atom % D).

## Preparation of dispersions

Sample preparation involved dissolving the polymer in water (either hydrogenated or deuterated) overnight whilst on a roller-mixer. All samples were made by addition of the required mass of SWCNTs to 2 ml of a polymer solution of the correct concentration to obtain a dispersion which was 0.3% wt SWCNTs, and 1% wt F127. This was followed by sonication (QSonica Q125) in pulsed mode at 57% max power for 1 hr. The samples were then centrifuged for 40 min at 20800 g, and the top  $\sim 1.5$  ml of the resulting supernatant was removed for use in scattering experiments. It is important to note that the SWCNT concentration of 0.3% wt quoted is not the final concentration, but rather is the concentration calculated before purification by ultracentrifugation. It is estimated from absorption measurements that  $\sim 1/3$  of the SWCNTs remain dispersed after purification, a relatively high concentration thought to be a consequence of the high purity of SWCNTs used.

## Absorption Spectroscopy

Absorption spectroscopy was performed on a HP/Agilent 8453 spectrophotometer over the range 400-1100 nm. Samples were diluted by a factor 30 with deionised water and run in square quartz cells with a 10 mm path length. Background water absorption was subtracted from all data.

## Small-Angle Neutron Scattering

Small-angle neutron scattering experiments were performed on the SANS2D small-angle diffractometer at the ISIS pulsed neutron source (STFC Rutherford Appleton Laboratory, Didcot, UK). A collimation length of 4 m and an incident wavelength of 1.75 - 16.5 Å were used. Data were measured simultaneously on two 1 m<sup>2</sup> detectors to give a Q range of 0.0045 - 1.92 Å<sup>-1</sup>. The small-angle detector was positioned 4 m from the sample and offset vertically 60 mm and sideways 100 mm. The wide-angle detector was positioned 2.4 m from the sample, offset sideways by 980 mm and rotated to face the sample. The beam diameter was 8 mm. Each raw scattering data set was corrected for the detector efficiencies, sample transmission and background scattering and converted to scattering cross-section data ( $\delta\Sigma/\delta\Omega$  vs. Q) using instrument-specific software.<sup>8</sup> These data were placed on an absolute scale (cm<sup>-1</sup>) using the scattering from a standard sample (a solid blend of hydrogenous and perdeuterated polystyrene), in accordance with established procedures.<sup>9</sup>

Samples were studied in 2 mm or 1 mm square quartz cells depending on the D<sub>2</sub>O/H<sub>2</sub>O content. All samples were studied below the critical micellisation temperature (CMT) to minimise scattering from the bare polymer. For an F127 concentration of 1% w/v, as used here, the CMT is 24 °C.<sup>10</sup> Therefore, samples were studied at 15 °C. All data sets had background solvent scattering subtracted.

In order to ensure the F127/SWCNT samples contained the same amount of carbon as each other (to simplify the SANS data analysis), the samples were made from F127/SWCNT/D<sub>2</sub>O and F127/SWCNT/H<sub>2</sub>O stock solutions which were mixed together in the correct proportions. The stock solutions were made as described previously, to give a total volume for the stock solution of over 1 mL. The concentrations of the two stock solutions were then compared using absorption spectroscopy, and the more concentrated D<sub>2</sub>O solution was diluted to the same concentration as the H<sub>2</sub>O stock solution dilution with a 1% F127 solution until the absorption spectra of the two stock solutions matched.

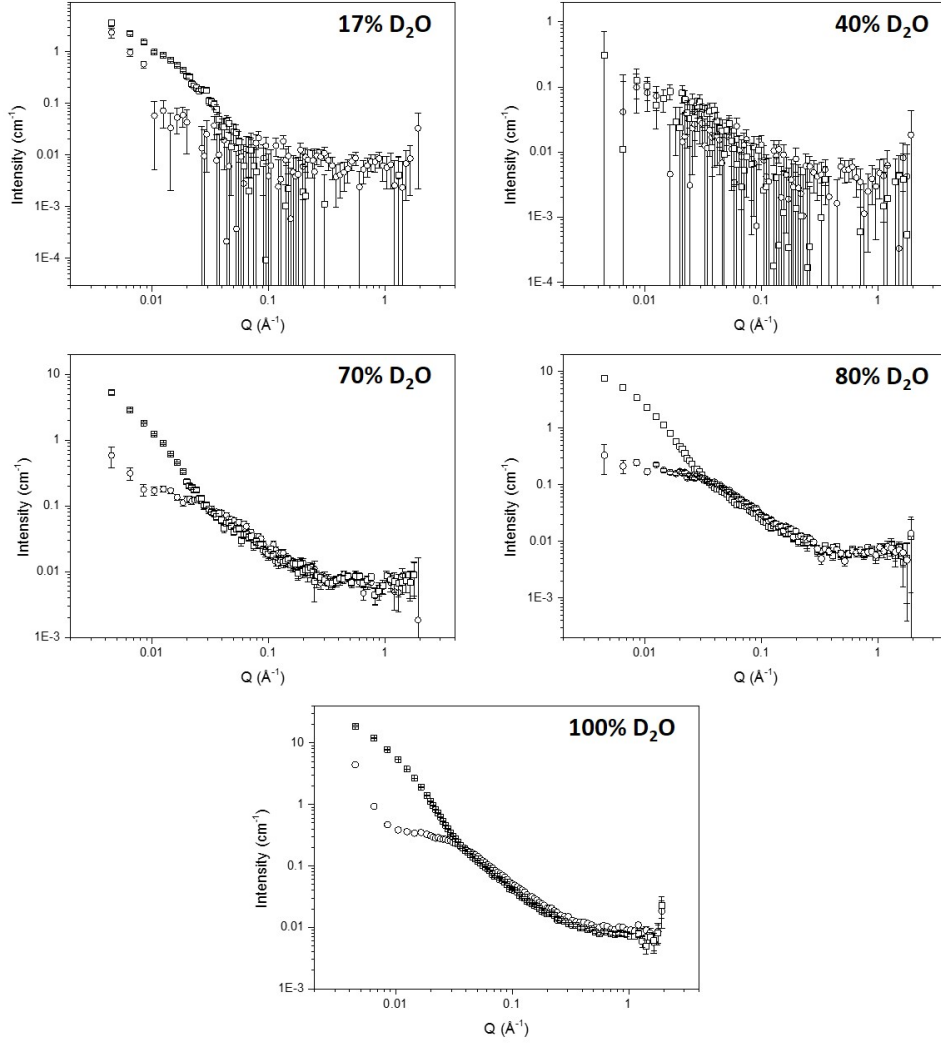
# Results and discussion

## Small-angle neutron scattering

The scattering patterns from dispersions of F127 polymer along with the F127/SWCNT data at the contrasts studied are given in fig. 1. As all dispersions were studied below the CMT of the polymer, the F127 did not form micelles and was instead present as free polymer chains, and thus the scattering contribution from the F127 itself was relatively small. At low  $Q$  values, the data for the F127/SWCNTs has a higher scattering intensity than the F127, however at high  $Q$  the curves have a very similar shape, suggesting that the scattering at high  $Q$  is dominated by the free F127 molecules. The curves for F127/SWCNTs tend to be at a lower intensity than the F127 alone at higher  $Q$ , suggesting that some of the F127 has adsorbed onto the SWCNT surface, which is thus affecting the scattering intensity at this  $Q$  range. The scattering data shows the highest intensity scattering at 100%  $D_2O$ , as expected, with 80% and 70%  $D_2O$  data both showing scattering of lower intensity than the full contrast data. The minimal scattering for our samples is seen at 40%  $D_2O$ , with some scattering seen at the lowest  $Q$  values for the 17%  $D_2O$  data (the match point of the F127), corresponding to the scattering of the nanotubes themselves with the F127 adsorbed layer matched to the solvent.

Data for F127 data were fit to a Debye-Guinier model for free polymers, which was then subtracted from the F127/SWCNT data. Detail about the fitting procedure is given in the supporting information to this paper. Data for SWCNT/F127 showed lower intensity scattering at high  $Q$ , so only 75% of the F127 Debye-Guinier fit was subtracted from the F127/SWCNT data to account for F127 adsorption onto SWCNTs, and the resulting scattering curves are shown in fig. 2.

The scattering patterns of the F127/SWCNT samples at different contrasts are shown in fig. 2. The scattering results presented here show that for the F127/SWCNT samples, the minimal scattering is seen at 40% SWCNT, as would be expected for a core-shell cylinder

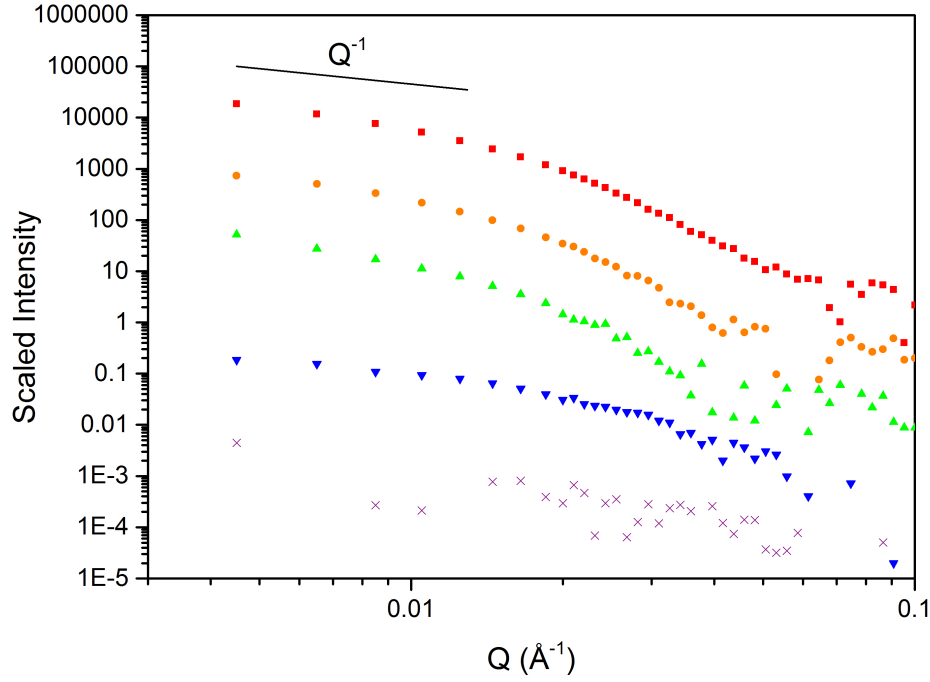


**Figure 1:** SANS scattering curves from dispersions of 1% w/w F127 (○) and 1% w/w F127 with 0.3% w/w SWCNTs (□)

of this type. The F127 alone is contrast matched at 17% D<sub>2</sub>O, the data for which is shown in fig. 1, and at this contrast the F127/SWCNT data shows a  $Q^{-1}$  power law at low  $Q$ , indicating rod-shaped objects are present.

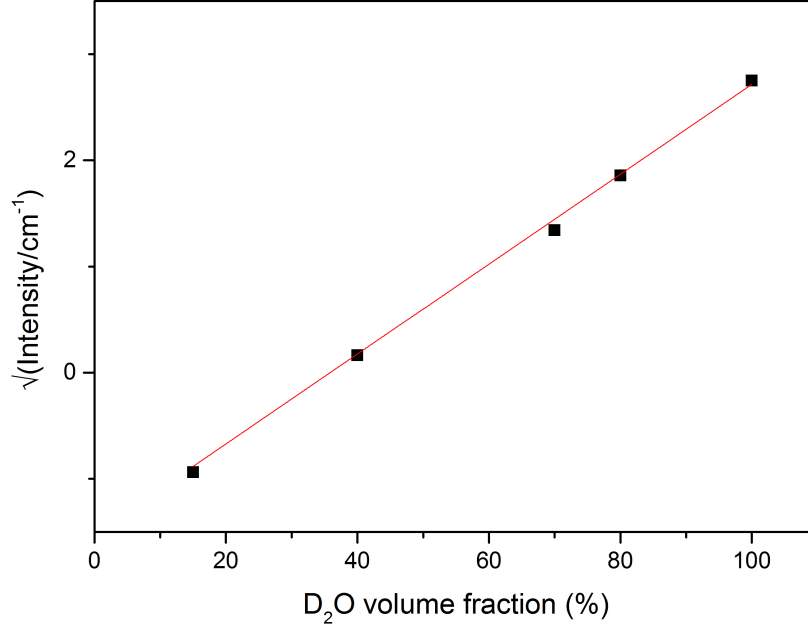
A contrast match plot for the F127/SWCNT data was made by taking the intensity of the SWCNT/F127 scattering at a  $Q$  value of  $0.0085 \text{ \AA}^{-1}$ , and subtracting the incoherent background and the F127 scattering at this contrast. The resulting contrast variation graph is shown in fig. 3. The data point at 17% D<sub>2</sub>O was beyond the contrast point, and thus had





**Figure 2:** SANS data from F127/SWCNT systems at various contrasts, with background  $D_2O$  and  $0.75 \times$  the F127 scattering subtracted, after shifting data sets for clarity. Each data set was shifted by a factor of 10 away from the data set next to it.  $D_2O$  content: 100% (■); 80% (●); 70% (▲); 40% (×); 17% (▼).

an intensity above that of the 40%  $D_2O$  data. Ideally, two separate lines would be drawn (above and below the match point) in order to find the x-intercept and thus the contrast match point, however in this case only one of the contrasts studied was at a  $D_2O$  composition below the match point. Thus, the intensity value at 17%  $D_2O$  was multiplied by a factor of -1 to enable one straight line to be drawn. The data shows a good fit to a straight line, and it can be concluded that a volume fraction of 36%  $D_2O$  would be required in order to obtain the minimal scattering from this system. This is in contrast to results reported by Granite et al., who observed a minimal scattering at 70%  $D_2O$ . Subtracted data shown in fig. 6 shows that the scattering for the SWCNTs shows a  $Q^{-1}$  power law at low values of  $Q$ , whereas Granite et al. reported a higher power law relation, attributed to branching of



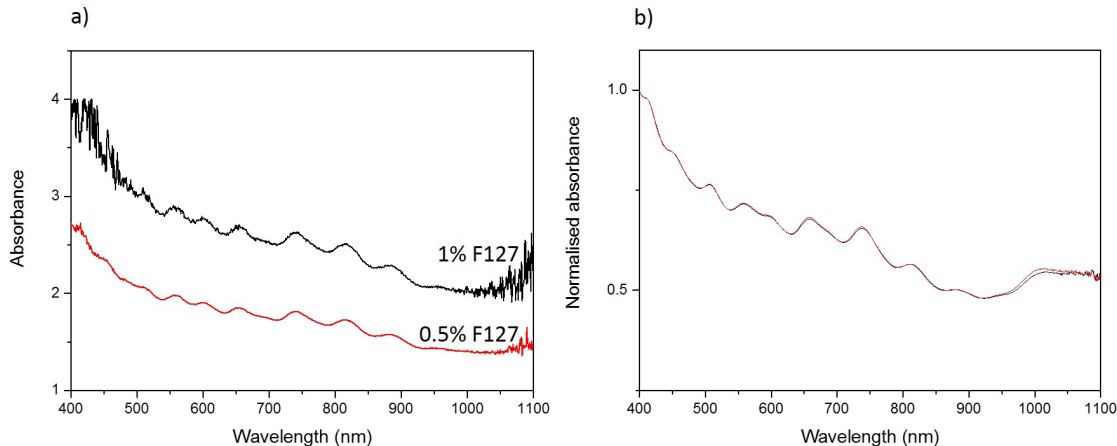
**Figure 3:** Contrast match plot for F127/SWCNT samples run at different contrasts. The intensity at  $Q = 0.0085 \text{ \AA}^{-1}$  was used for every contrast studied, and the background scattering and F127 scattering at this  $Q$  value were subtracted.

SWCNTs and a wide range of SWCNT sizes. It is thus possible that dispersions made here have a lower degree of SWCNT branching, and are thus more amenable to being fit to a core-shell cylinder model.<sup>7,11,12</sup>

Judging from previous experiments looking at the dispersions using TEM (shown in the supporting information to this paper) it is unlikely that the SWCNTs will be present as individual tubes, although some of them may be. Rather, the majority of the nanotubes will be present in small bundles. TEM images also show that residual catalyst particles are present in the dispersions, however this is not thought to affect the SANS results, as explained further in the supporting information to this paper.

It has been reported that the degree of bundling in a sample can be detected by UV-vis-NIR spectrophotometry.<sup>13</sup> SWCNT bundling causes broadening and red-shifting of the peaks in the UV-vis-NIR spectra.<sup>14</sup> The absorption spectra obtained from our samples, shown in

fig. 4, have peaks which are not as sharply defined as the single SWCNT peaks in Backes et al.'s work, implying some degree of bundling is present. However, absorption spectra of the samples are similar to those seen by Yurekli et al., who took these as evidence that the SWCNTs were present as individual tubes rather than bundles.<sup>3</sup> The absorption spectra of the F127/SWCNT systems in D<sub>2</sub>O and H<sub>2</sub>O were scaled down by dividing all absorbances by the absorbance obtained at 400 nm. Thus the peaks of the absorption spectra can be directly compared, and it is clear that the spectra show very similar absorbance peaks, suggesting that the level of debundling is similar in both samples.



**Figure 4:** Absorption spectra of F127/SWCNT/D<sub>2</sub>O (black line) and F127/SWCNT/H<sub>2</sub>O (red line) dispersions, with both the original spectra (a) and the spectrum with the absorbances normalised at 400 nm (b).

The model used to fit the data presented here is a core-shell cylinder model, simpler than models previously used to fit such data and the scattering length densities (of the core and shell) are averaged with the relative amount of water thought to be present, as explained in the supporting information.

We have used a core-shell cylinder model to fit the scattering data of the decorated SWCNT cylinders at all contrasts studied, using the SasView fitting programme, developed at NIST.<sup>15</sup> This model consists of a core (with an SLD calculated as a mixture of the SLD of graphene (calculated to be  $7.4 \times 10^{-6} \text{ \AA}^{-2}$ ) and the scattering length density of the appropriate solvent mixture, and a homogeneous shell consisting of a diffuse F127 layer. In

order to simulate the inhomogeneity of the F127 adsorbed layer in this simple model, a log-normal polydispersity for thickness has been introduced into the scattering of the shell. The polydispersity function used also serves to account for the instrument resolution, as the Q-dependency of the data is weak and smearing due to polydispersity is much greater than the effect of the instrument resolution.

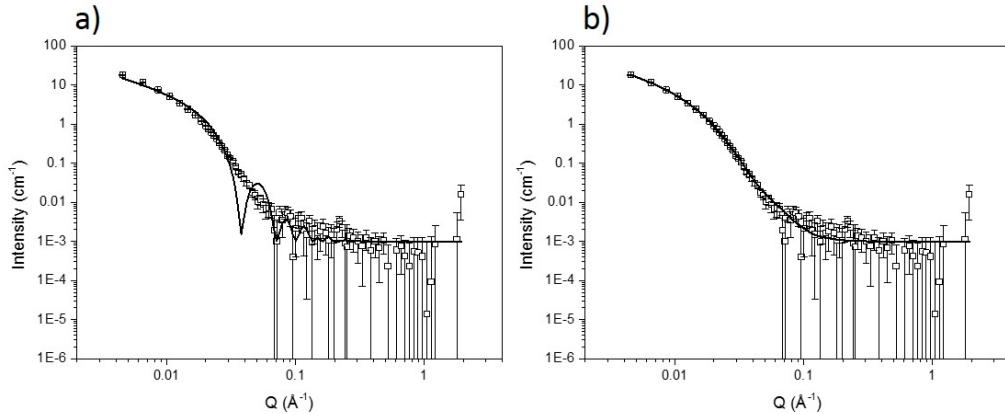
Adsorbed layers of F127 have been widely studied, and the values obtained for the size and composition of these adsorbed layers give an idea of what the contribution to scattering from the adsorbed layer in the system studied here is likely to be. Granite et al. estimated that the adsorbed layer of F127 on their SWCNT samples had a thickness of 120 Å and a volume fraction of 0.049, which corresponds to an adsorbed amount of 1.80 mg m<sup>-2</sup>.<sup>7</sup> Malmsten et al. studied F127 adsorption at silica surfaces, and found the hydrodynamic thickness of the layer to be 20-60 Å.<sup>16</sup> Assuming a thickness of 60 Å, the volume fraction of F127 in the layer would need to be 0.07 in order to match the adsorbed amount of 0.4 mg m<sup>-2</sup>. Lin and Alexandridis measured an F127 layer thickness of 71 Å on carbon black, and the adsorbed amount to be 0.543 mg m<sup>-2</sup>, while Nelson and Cosgrove found the adsorbed layer of F127 onto Laponite to have a thickness of only 35 Å, with an adsorbed amount of 0.87 mg m<sup>-2</sup>. It is therefore expected that the adsorbed F127 layer will have a relatively low volume fraction, however the thickness could be anywhere in a wide range of reported values.<sup>17,18</sup> The adsorbed layer thickness must be less than the extended chain length of one of the PEO blocks (350 Å based on a monomer chain length of 3.5 Å<sup>19</sup>).

The fitting procedure used here consists of several stages:

1. The thickness of the adsorbed layer can be approximated using the scattering data obtained at 100% D<sub>2</sub>O. We have assumed that the core has a high SLD (as we think it mainly consists of carbon, with some solvent present from the opening of the tubes during ultrasonication) and a relatively small radius. The shell is composed of a diffuse layer which has a high solvent composition. Therefore, at the highest D<sub>2</sub>O content, the

scattering length density of the shell will nearly match the scattering length density of the core, and fitting the shape of this data will depend mainly on the thickness of the adsorbed layer.

Rather than using a model in which the adsorbed layer is ‘fuzzy’, it was decided to use a simple model in order to keep the number of parameters at a minimum. Adding polydispersity to the thickness of the adsorbed layer has a similar effect to using a fuzzy layer model, and decreases the polymer segment density away from the core. This can be seen in fig. 5. Thus a value of 61 Å was obtained for the F127 adsorbed layer, with a log-normal polydispersity of 0.4, the distribution of which is given in the supporting information. By integrating over the log-normal distribution, a mean thickness (taking into account the polydispersity) of 65 Å was obtained.



**Figure 5:** Fitting procedure: thickness a) no polydispersity b) polydispersity added to the thickness of the adsorbed layer

2. Once the thickness had been established, it could then be used to calculate the volume fraction of F127 in the adsorbed layer. The scattering intensity of SWCNT/F127 data at high  $Q$  was lower than F127 alone at every  $H_2O/D_2O$  composition, which was interpreted as being caused by a fraction of the F127 as having been removed from the solution by adsorption onto SWCNTs.
3. Lastly, fig. 3 shows that the contrast match point for the F127/SWCNT scattering

occurs at 36% D<sub>2</sub>O. The thickness and the volume fraction of the adsorbed layer is known, therefore the scattering length density of the SWCNT can be calculated so that the scattering from the core and the shell cancel each other out at this D<sub>2</sub>O composition. Preliminary data fitting shows that the best fits are obtained with a relatively small core radius and a low volume fraction of water in the SWCNT core.

We can use the relationship between the scattering of the core and shell to fit the data at different core radii and core SLDs (assuming different amounts of solvent are present in the core each time), in order to find the best fit across all contrasts studied. At the contrast match point, shown in fig. 3 to be 36% D<sub>2</sub>O, must satisfy the condition given in eq. (1).

$$\rho_{core}a_{core} + \rho_{shell}a_{shell} = 0 \quad (1)$$

We have calculated the contribution to the overall scattering from the inner SWCNT core and the outer adsorbed layer, based on the fitting parameters given in table 1. With an inner radius of 10 Å, an F127 shell thickness of 61 Å, a volume fraction of water in the shell of 0.93 and a volume fraction of water in the core of 0.2, the calculated match point would be 37% D<sub>2</sub>O, a value which is very close to the value estimated from fig. 3.

Fitting the data to a core-shell cylinder model gives reasonable fits across all contrasts studied, as shown in fig. 6. The fits show the core to be a small SWCNT bundle surrounded by a diffuse, polydisperse layer of F127, with a thickness of 61 Å. The parameters used in fitting the data to a core-shell cylinder model are given in table 1. The data at 17% D<sub>2</sub>O could be fit by including a small amount of scattering in the shell (i.e. the shell was slightly off contrast), to account for imperfect contrast matching of the F127. Polydispersity was added to the thickness of the adsorbed layer, in order to approximate the effect of the PEO and PPO blocks of the polymer. The data for the system at 40% D<sub>2</sub>O has a very

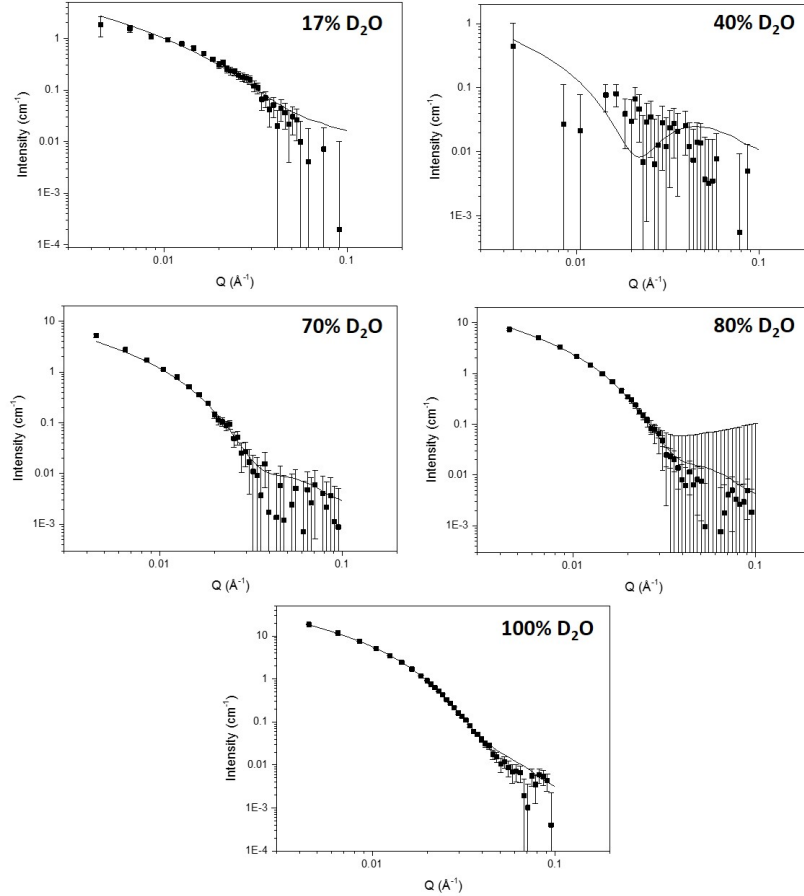
low scattering intensity and large error bars associated with it, and thus fitting this data is difficult. However, this is a key piece of evidence to support the core-shell cylinder model, as it shows that the system is close to the match point at this D<sub>2</sub>O content.

**Table 1:** Table of parameters used to fit SWCNT/F127 data to core-shell cylinder model across all contrasts. The values for  $\rho_{solvent}$  are as follows: 17 % D<sub>2</sub>O,  $0.5 \times 10^{-6} \text{\AA}^{-2}$ ; 40 % D<sub>2</sub>O,  $2.2 \times 10^{-6} \text{\AA}^{-2}$ ; 70 % D<sub>2</sub>O,  $4.27 \times 10^{-6} \text{\AA}^{-2}$ ; 80 % D<sub>2</sub>O,  $4.96 \times 10^{-6} \text{\AA}^{-2}$ ; 100 % D<sub>2</sub>O,  $6.36 \times 10^{-6} \text{\AA}^{-2}$ .

Parameter	
Water in core / vol %	20
Water in shell / vol %	94
Radius/ $\text{\AA}$	10
Shell thickness / $\text{\AA}$	61
Polydispersity of thickness	0.43
Volume fraction	0.049

Based on the fits obtained here, the amount of F127 adsorbed was calculated and compared with the amount of F127 which had been assumed to be adsorbed to the SWCNT surface based on the subtracted surfactant data. The volume fraction of decorated cylinders, thickness of the adsorbed layer and the radius of the SWCNT bundle obtained from the fits were used to calculate the total length of cylinders in the sample. The total amount of F127 used can then be calculated using the volume fraction of F127 in the adsorbed layer. Using this method, the total amount of adsorbed F127 is calculated to be 0.0022 g adsorbed F127 per cm<sup>3</sup> sample, compared to 0.0025 g from the fraction of the F127 data which was subtracted. The agreement of these two values implies that the model used here represents the adsorbed amount of F127 well. It must be stressed that this value gives us the adsorbed amount per cm<sup>3</sup> of the dispersion, and not an adsorbed amount per unit of SWCNT area, which is calculated to be 1.3 mg m<sup>-2</sup>, based on the fit parameters in table 1. This is thought to be a reasonable value for the adsorbed amount when compared to values for adsorbed

amounts in the literature, mentioned earlier, particularly a value obtained by Granite et al. of  $1.80 \text{ mg m}^{-2}$ , and a value obtained by Lin and Alexandridis of adsorbed F127 onto carbon black of  $0.543 \text{ mg m}^{-2}$ .<sup>7,17</sup>



**Figure 6:** Scattering curves for F127-decorated SWCNTs at the five contrasts studied, with the core-shell cylinder fits described in table 1.

From experimental data studied here, SANS data fitting is consistent with small SWCNT bundles in solution (of radius  $10 \text{ \AA}$ ), surrounded by a diffuse, water-swollen F127 adsorbed layer (of thickness  $61 \text{ \AA}$ ), and an adsorbed amount of  $1.3 \text{ mg m}^{-2}$ . These results are in general agreement with the main conclusions of Granite et al., and the adsorbed amount is consistent with previously reported values for F127 adsorption on other substrates.<sup>17</sup> This finding is in contrast with previous work on the adsorption of small-molecule surfactants on SWCNTs, which are thought to form a dense and thin adsorbed layer on the surface of



SWCNTs.<sup>3</sup>

## Conclusions

Dispersions of SWCNTs dispersed with F127 Pluronic block copolymer were investigated using small-angle neutron scattering. In this work we have shown that our data agreed with predicted scattering for a SWCNT core surrounded by a diffuse polymer layer, with minimal scattering being seen at a D<sub>2</sub>O composition of 40%, as expected for core-shell cylinders of this type. The SANS data fitting is consistent with small SWCNT bundles in dispersion, stabilised with an adsorbed F127 layer which is extended (with a 61 Å thickness) and water-swollen (with a water content of 94% in the adsorbed layer).

Absorption spectra of the samples studied with SANS shows no differences between the peaks of the samples made in D<sub>2</sub>O compared to those made in H<sub>2</sub>O. The peaks seen in these spectra are consistent with a high degree of debundling, although we believe they are too broad for single tubes, consistent with the parameters obtained when fitting the SANS data using the core-shell cylinder model.

The adsorbed layer fit the core-shell cylinder model well, with the adsorbed layer having a thickness and volume fraction of F127 which fits with previous literature values. SWCNT/F127 samples were stable for many months after initial dispersion, hence F127 is a suitable steric stabiliser for SWCNTs. These results show that the analysis of F127 adsorption onto SWCNTs can be simplified by using a core-shell cylinder model to characterise the adsorbed layer, which could have wider applications for the analysis of other adsorbed molecules onto carbon nanotubes.

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## Supporting Information Available

This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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## Graphical TOC Entry

